A COMPARISON OF ELECTRICAL METHODS WITH CHEMICAL METHODS FOR THE ANALYSIS OF PICKLED HIDES

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ABSTRACT

Analyses for chloride, sulfate, total acid, calcium, and ammonia were performed on commercially prepared pickled hides and their expressed liquors by chemical and electrochemical methods. Data obtained with well equilibriated hides showed that specific ion electrodes, where available, gave values that reflected accurately the analyses obtained by chemical methods. Electrodialysis measurements gave the total electrolyte content.

INTRODUCTION

Specific ion electrodes capable of measuring the concentration of ammonium, chloride, hydrogen, and sodium ions in solutions have been developed which might possibly simplify the analysis of pickled hides. A flat-surfaced glass electrode and a chloride-sensitive electrode have been shown (1) to measure the pH and chloride ion concentration on the surface of experimental hides. However, the results obtained by these electrodes have never been compared with chemical determinations made on commercially pickled hides. At present the ammonium and sodium ion electrodes are not adaptable to surface measurements but could possibly be used to speed up the analysis of solutions pressed from pickled hides.

Total salt content of hides is usually determined by ashing a sample cut from the hide, but this value will not include volatile electrolytes and does not differentiate between sodium chloride, sodium sulfate, and calcium sulfate. More meaningful analysis can be made upon the solution pressed from pickled hides, and simple specific chemical tests adaptable to tannery use are available for determination of chloride, sulfate, ammonium, calcium, and hydrogen ions. The analytical values obtained with specific ion electrodes on the surface of the pickled hide and immersed in the expressed solution were compared with the specific chemical analysis values.

To determine whether the ions measured constituted the total electrolyte present in the pickled hides, the values were compared with the total electrolytes that can be determined by electrodialysis, using an electrodialysis cell (2) which is capable of studying both the solid hide sample and the expressed solution.

EXPERIMENTAL

Pickled hides obtained from commercial sources and stored in plastic bags for at least 30 days were sampled by die cutting to provide material for ash, moisture, and electrodialysis studies. For thin stock, two inch diameter discs were used for ash and moisture and one inch squares were used for electrodialysis. For measurements involving full thickness hide material, one-half inch diameter plugs were used. To obtain the expressed liquid, about 50 grams of the hide was folded and placed between heavy polyethylene sheeting in a laboratory size Carver† press. A pressure of 10,000 lbs. per sq. inch was used to press the liquid from the hide. The expressed liquid was shaken with an equal volume of chloroform to remove fatty materials before use for the analysis.

The pickled hides studied were domestic sheepskins, Nigerian sheepskins, grain splits, and full thickness cattlehides. These were obtained from a number of commercial tanneries.

Moisture and Ash Determination

Die cut pieces of the hide were weighed rapidly in platinum dishes and dried in a vacuum oven at 50°C., using a slow stream of dry air to sweep the evaporated moisture from the oven. The samples reached constant weight after 18 hrs. The difference in weight was recorded as moisture. The platinum dishes containing the dried material were then placed in a cold muffle furnace and heated slowly to 600°C. After six hrs. the ash was cooled and weighed. If the ash was gray or black colored, it was wet with a small amount of water, dried, and reashed. The final weight was recorded as ash. Duplicate samples were run and the results averaged.

The moisture content of the defatted pressed liquor was determined by placing a two ml. aliquot of the liquor in a large weighing bottle and drying it in a convection oven at 105°C. for 18 hrs. The loss in weight was recorded as moisture. Duplicate samples were run and the results averaged.

Determination of pH

A flat-surfaced glass electrode made by Radiometer, Inc., was used in conjunction with a Beckman frit junction calomel electrode and an Orion model 801 digital pH meter with automatic printout to determine the pH both on the hide surface and in the expressed solution. Both electrodes were firmly set on the hide

†Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

surface and loosely supported so that the weight of the electrode maintained a constant force on the hide piece to assure a reproducible contact. When positioned in this manner, reproducible values were obtained within a few minutes.

The expressed solution was also tested with Duotest Indicator paper, which has an accuracy of 0.3 units.

Determination of Chlorides

Total chlorides were determined using a chloride-sensitive electrode and also by the Mohr chemical method. The electrode was a Beckman silver billet electrode plated with silver chloride. The cylindrical sides of this electrode were covered with polyethylene or glass fiber electrical tape to prevent interactions on the side of the electrode when only the flat tip is being used on the surface of a hide. The plating was made by immersing the electrode in saturated potassium chloride solution with a strip of silver ribbon as the second electrode and applying alternately for 30-second intervals three volts of positive or negative potential. The response of the electrode was determined with standard sodium chloride solutions and the values of the test solutions obtained by interpolation from a graph of the standard values. When used on a hide surface the electrode was paired with a frit junction calomel electrode and firmly set on the hide surface. The electrodes must be loosely supported so that the weight of the electrode maintains a constant force on the hide piece to assure reproducible contact.

The Mohr method for chloride determination was used on the expressed liquor. Two ml. of the expressed liquor was titrated with standard 0.10 N silver nitrate. Potassium chromate was the indicator.

Determination of Sodium

A glass electrode made by Beckman and designed to be especially sensitive to sodium ion activity was used for this study on the expressed liquors. This electrode must be used at a high pH to suppress hydrogen ion effects. A method has been developed (3) to do this by using two ml. of the sample after diluting two ml. to 200 ml. with water and 18 ml. of 0.1 M trishydroxymethylaminomethane (tris) buffer at pH 8.0. After mixing and equilibrating the solution, the millivolt reading was recorded. The rate of equilibration varies with the difference in concentration from the previous sample. The electrode is kept in a salt solution of approximately the same concentration as the samples when not in use. The electrode was paired with a fiber junction calomel electrode and these were wiped with a Kimwipe between samples, since rinsing with water would increase the equilibration time greatly. The response of the electrode was determined with standard sodium chloride solutions in the tris buffer and the values of the test solutions obtained by interpolation from a graph of the standard values.

Determination of Ammonium Salts

Ammonium salts in the expressed liquor were determined by use of an ammonia electrode and by distillation of the alkalized solution. The Orion ammonia electrode needs no additional reference electrode. Two ml. of the expressed solution was diluted to 200 ml., 100 ml. of this was pipetted into the measuring beaker, and one ml. of ten molar sodium hydroxide was added. A magnetic stirrer was used to mix the solution. After 30 seconds, the millivolt reading was recorded, ten ml. of a standard ammonium chloride solution was added, and the millivolt reading again taken after 30 seconds. The difference in potential noted is reduced to a factor by use of a known addition increment table and the concentration of the ammonia is calculated from this and the concentration of the standard used.

For the distillation of the ammonia, two ml. of the expressed solution was introduced into a standard semimicro Kjeldahl distillation apparatus, made alkaline with ten ml. of concentrated sodium hydroxide, and distilled for five minutes. The liberated ammonia was trapped in boric acid and titrated with 0.02 N hydrochloric acid, using an indicator composed of two parts methyl red and one part methylene blue.

Determination of Total Sulfates

Two ml. samples of the expressed liquor were titrated with a standard 0.1 M barium chloride solution. After each addition, the precipitate was allowed to settle and a drop of the supernatant was applied to a spot of rhodizonic acid solution on a filter paper. The indicator changes from yellow to red at the end point (4).

Determination of Acidity

The total acidity was determined by titrating two ml. of the expressed liquor with standard 0.01 N sodium hydroxide, using phenolphthalein as indicator. For the calculations, this free acid was assumed to be entirely sulfuric acid.

Determination of Calcium

Calcium was determined by an EDTA titration method (5). Two ml. of the expressed liquor was titrated with standard 0.05 N EDTA (disodium dihydrogen ethylene-diaminetetraacetate) using Cal Ver II (Hach Chemical Co., Ames, Iowa) as indicator.

Calcium was also determined on the ashes obtained from the die cut hide samples. The ash was dissolved in one ml. of 1.0 N hydrochloric acid and diluted to 200 ml. Fifty ml. was used for the titration described above.

Electrodialysis of Expressed Liquor and Hide Samples

The electrodialysis cell and its operation have been previously described (2).

One inch squares or one-half inch diameter circles of the pickled hides, or 0.3 ml. of the expressed liquor, were placed in the center compartment, which was then filled with distilled water to the top of the electrodes. The center compartment also contained a cooling coil of fine plastic tubing through which cooling water was pumped. A voltage (about ten volts) sufficient to produce a current of 150 milliamperes was placed across the electrodes in the two outer compartments. Cold distilled water was pumped through the two outer compartments to keep them cool and to remove the electrolytes which were drawn to these compartments. The solution from the anion compartment (containing the positive electrode) contained chlorine, which was trapped in a measured volume of standard 0.1 N alkali in the anion receiver. The solution from the cation compartment was collected in the cation receiver.

The anion solution was titrated with 0.1 N hydrochloric acid to pH 8.7 so that only the excess alkali would be measured. The amount of added alkali not titrated was equivalent to the anions produced in the electrodialysis. The cation solutions were titrated with the standard acid to pH 5.0 so that carbonates from the air would not affect the results. The amount of acid used was equivalent to the amount of cations formed in the electrodialysis. The two end points used above were found to be necessary in the original calibration of the cell with known electrolyte solutions.

RESULTS AND DISCUSSION

Representative values obtained with the flat-surfaced glass electrode on the surface of three types of pickled stock and immersed in the solution expressed from the same sample are compared in Table I. Values obtained with a two-color indicator paper in the expressed solution are also given as a comparison.

TABLE I

pH DETERMINATION

	Electrode		Indicator Paper
	Surface	Express Liquid	Express Liquid
Sheepskin	1.39	1.32	1.3
Grain Split	1.94	1.92	1.9
Steerhide	2.18	2.17	2.2

The agreement is very good. It probably takes a few minutes longer to measure the pH on the surface of the hide than it does to measure it in the solution, but the time and effort of pressing out the solution would be saved.

Representative values obtained for three types of pickled stock with the chloride-sensitive electrode are presented in Table II. There is very good agreement between the surface and solution measurements for the sheepskin and grain split stock and these values were only slightly higher than the values obtained by the chemical method. The steerhide values for the surface and expressed liquor are considerably different, but they are on both sides of the chemically determined

TABLE II

CHLORIDE DETERMINATIONS AS PERCENT SODIUM CHLORIDE

	Electrode		Chemical	
	Surface	Express Liquid	Express Liquid	Difference (%)
Sheepskin	17.3	17.3	16.7	+3.6
Grain Split	13.4	13.5	12.9	+4.6
Steerhide	7.2	6.5	6.9	−5.8 (Liquid) +4.3 (Surface)

value and their percentage difference from the chemically determined value is of about the same order as those for the sheepskin and grain split. The rate of equilibration for the chloride ion electrode is slow, especially if it is subjected to large changes of chloride ion concentration. An average of ten minutes equilibration time was required for each sample. Slightly less accurate results could be obtained if values were read at an arbitrarily set shorter time. Another problem with the chloride ion electrode is the solubility of the silver chloride in the strong salt solutions. This necessitates replating the electrode about twice a day.

The results obtained for the ammonium ion electrode are presented in Table III. Good agreement was obtained between the electrode values and values found by the distillation of the ammonia in a semimicro Kjeldahl distillation apparatus.

TABLE III

AMMONIUM ION DETERMINATION

(Milliequivalents per Liter)

Hide Type	Electrode	Distillation and Titration	Difference (%)
Sheepskin	25	24	4.2
Grain Split	113	110	2.7
Steerhide	170	165	3.0

The electrode values were about three percent higher than the distillation values. The electrode values are obtained more rapidly than the distillation values; however, a high impedance meter sensitive to 0.1 millivolt is required.

A comparison of the sulfate ion concentrations in pickled hides is complicated by the fact that there are at least four sources of sulfate ions present: sodium sulfate and ammonium sulfate used to control swelling and delime the hides prior to pickling, calcium sulfate formed from residual lime in the hide, and the sulfuric acid added to produce the acidity. The amounts of sulfate ion found for these various sources in the three types of pickled hides are presented in Table IV. The sum of the sulfate ion concentrations for the ammonium, calcium, and free acid present was subtracted from the total sulfate found by the barium chloride titration to obtain a value for the amount of sodium sulfate that could

TABLE IV

SULFATE ION DETERMINATIONS
(Milliequivalents per Liter)

Hide	NH_4^+	Ca^{+2}	Acid	Sum	Total Sulfate	Other Sulfates (as Na_2SO_4)
Sheepskin	24	50	33	107	123	16
Grain Split	112	46	23	181	308	127
Steerhide	165	35	41	241	418	177

be present. This may not be entirely sodium sulfate since the value is obtained by difference. The amount of sulfate from calcium and acid is comparatively constant in the three types of hides, but the amounts of ammonium sulfate and sodium sulfate vary widely. This probably reflects the degree of washing after the deliming and bating steps.

The sodium ions present come chiefly from the sodium chloride or salt added to control swelling and the sodium sulfate which is carried over from the bating process. Table V gives a comparison of the amounts of sodium attributable to

TABLE V

SODIUM ION DETERMINATIONS AS PERCENT SODIUM

	From NaCl	From Na_2SO_4	Total	By Electrode	Difference (%)
Sheepskin	6.57	0.03	6.60	6.69	1.4
Grain Split	5.08	0.18	5.26	5.43	3.2
Steerhide	2.72	0.38	3.10	2.99	3.5

sodium chloride and sodium sulfate with the amount of sodium detected by the sodium specific electrode. The amount of sodium sulfate present was calculated by subtracting the amounts of ammonium sulfate and calcium sulfate present, assuming that the ammonium and calcium chemically determined are present as sulfate. The remainder is assumed to be sodium sulfate. The chlorides are then assumed to be sodium chloride. The percent differences are small and indicate that the electrode can be used to determine the amount of sodium present in the expressed pickle liquor.

Since analyses have been made only for the ions suspected of being present, it is of interest to know how the sum of these ions compares with the total amount of electrolyte present. To do this, an electrodialysis cell developed earlier (2) was used to determine the total amount of anions and cations that could be removed by an electric current. The details of one of these comparisons for the expressed liquor are given in Table VI. During the electrodialysis, the hydrogen ions are liberated as hydrogen and no attempt has been made to trap this; therefore, the free sulfuric acid is listed as contributing only sulfate ions to the total anions determined. The ammonium ions which would come from the ammonium sulfate and be released at the cathode will be turned to ammonia in the alkaline

TABLE VI

DETAILS OF COMPARISON OF ELECTRODIALYSIS VALUES WITH CHEMICAL ANALYSIS VALUES FOR EXPRESSED LIQUORS

(Milliequivalents per Liter)

Source	Cations	Anions
NaCl	2440	2440
H_2SO_4		23
$(NH_4)_2SO_4$		112
$CaSO_4$	46	46
Na_2SO_4	127	127
	2613	2748
Electrodialysis	2740	3030
Difference	127	282

solution produced at the cathode. These ions could have been trapped by making the cation receiver acid but this was not done for these experiments, so that they will not be determined in the titration for total cations. Therefore, in Table VI the ammonium sulfate is listed as contributing only sulfate anions. The other salts present contribute equal equivalents of anions and cations. The total amount of cations recovered by electrodialysis is slightly greater than the total amount

of cations estimated by the chemical determinations. Also, the total number of anions found in the case of pickled stock is always appreciably greater than the total number of cations found and significantly greater than the amount of anions found by the chemical determinations made. This is shown for a number of different types of pickled stock in Table VII. For these samples the electrodialysis value for the cations is approximately five percent greater than for the combined analytical values. The difference for the anions is about twice this.

TABLE VII

COMPARISON OF ELECTRODIALYSIS VALUES WITH CHEMICAL ANALYSIS VALUES FOR EXPRESSED LIQUORS

(Milliequivalents per Milliliter)

Hide Type	Cations			Anions		
	Electro-dialysis	Analysis	Diff. (%)	Electro-dialysis	Analysis	Diff. (%)
Sheepskin	3.34	3.28	2.0	3.50	3.34	5.0
Sheepskin	2.06	2.01	2.4	2.39	2.18	9.6
Split-grain	2.74	2.61	4.9	3.03	2.75	10.3
Split-grain	2.70	2.54	6.0	2.92	2.68	9.0
Split-grain	2.12	2.10	0.7	2.50	2.32	7.8
Cattlehide	2.25	2.14	5.4	2.47	2.30	7.3
Cattlehide	1.50	1.54	−2.3	1.80	1.59	13.0

It thus appears that the chemical analyses used account for most of the cations present, but there must be some anions present which are not determined by the specific chemical tests used.

The electrodialysis results obtained on pieces of pickled hide are more difficult to interpret, since the chemical analysis cannot be made directly on the piece. Because of the difference between the electrodialysis values and the chemical analysis values obtained on the expressed solution, the first comparison was made by comparing the electrodialysis value on the piece with the electrodialysis value on an amount of the expressed solution with a water content equivalent to the moisture content of the hide. A comparison of this type is shown in Table VIII. There is very little agreement either for the anions or cations, except for a very few samples. The agreement between duplicate samples, however, is very good, indicating that the electrodialysis gives quite reproducible results.

When the ratios of the piece values to the solution values are determined as in Table IX, some of the samples fall within a narrow range of anion values. The cation values, however, appear to be quite generally distributed. Both the anion and cation ratios are less than one, indicating there must be some absorbed

TABLE VIII

COMPARISON OF ELECTRODIALYSIS VALUES OBTAINED ON HIDE PIECES AND EXPRESSED SOLUTION

(Milliequivalents per Gram of Water Content)

Hide	Cations		Anions	
	Piece	Solution	Piece	Solution
Sheepskin	2.85	3.65	3.34	3.81
	2.78	3.65	3.34	3.82
Sheepskin	1.88	2.19	2.11	2.52
	1.95		2.20	
Grain Split	1.67	2.27	2.04	2.66
	1.63	2.24	2.26	2.55
Grain Split	1.50	1.57	1.74	1.76
Cattlehide	1.03	1.55	1.57	1.84
	0.93		1.33	
Cattlehide	1.25	1.71	1.80	1.93
	1.33		1.80	
Cattlehide	1.45	2.42	2.01	2.63
	1.27		1.47	

TABLE IX

COMPARISON OF RATIOS OF ELECTRODIALYSIS VALUES

Hide	Piece Value / Solution Value		Cation Value / Anion Value	
	Cations	Anions	Piece	Solution
Sheepskin	0.77	0.87	0.84	0.96
Sheepskin	0.88	0.86	0.89	0.87
Grain Split	0.73	0.82	0.77	0.87
Grain Split	0.86	0.89	0.91	0.95
Cattlehide	0.63	0.79	0.68	0.84
Cattlehide	0.75	0.93	0.72	0.89
Cattlehide	0.56	0.66	0.79	0.92
	5.18	5.82		
Average	0.74	0.83		

water in the piece which cannot act as solvent water. The amount varies from sample to sample but from the average of all the cation ratios (0.74) it would appear that approximately 25 percent of the water is probably bound water and is not available for dissolving or holding ions from the solution. In most cases

the anion ratios are higher than the cation ratios, which would be an indication that some anions are being bound to the hide. Information on the nature of the excess of anions both in the expressed liquor and in the piece is required before a more detailed analysis of the electrodialysis values on the piece can be made.

The ratio of the cations to anions for the piece has about twice the variation of the ratio for the expressed solution, indicating that electrolyte variations within the hide are greater than in the solution. An examination of these phenomena under more strictly controlled conditions where all the possible added electrolytes are known will be necessary to determine whether these differences are actual or are due to experimental error.

CONCLUSIONS

A surface glass electrode can measure the pH of the surface of a pickled hide. If the hide piece has reached equilibrium, the surface value will be the same as the value of the expressed solution.

A flat-surfaced, chloride-sensitive electrode can measure the concentration of chloride ion on the surface of a pickled hide. The response is slower than for the pH determination, and although the surface value will be the same as the value obtained on the expressed solution, when the hide is at equilibrium this value is slightly higher than that obtained by the Mohr titration.

The sodium sensitive glass electrode can measure the sodium ion concentration of the solution pressed from pickled hides. The response of the electrode is slower than for pH electrodes, with the response time increasing with magnitude of the change in concentration to which the electrode is exposed.

The ammonia electrode will accurately measure the concentration of ammonium ions in the expressed solution from pickled hides. Excellent response time is obtained by using the known addition method of measurement.

Electrodialysis of the expressed liquor from pickled hides indicates that most of the electrolytes present can be determined by analysis for chloride, total sulfate, total acid, ammonia, and calcium. The agreement for cation recovery is better than for anion recovery, indicating the presence of other anions.

Electrodialysis has produced results which may be used for detecting differences in pickled hides. A comparison of the ratio of cations for the piece and the solution made on a water content basis indicates that a measure of the bound water may be possible. Also, the ratio of cations to anions may lead to a determination of the amount of acid bound to the protein. Variations of cation and anion contents in the piece appear to be greater than the variation in the expressed liquid.

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DISCUSSION

DR. THOMAS C. THORSTENSEN (Thorstensen Laboratories): Thank you very much, Helen, for this most interesting paper. On behalf of the Association, I present to you this Certificate of Appreciation.

MISS HELEN A. GRUBER (Eastern Regional Research Center, USDA): Thank you.

DR. THORSTENSEN: The discussion leader for this paper will be Dr. Ross G. Donovan of Canada Packers Limited.

DR. ROSS G. DONOVAN (Canada Packers Limited): In the process of developing new methodology for the tannery laboratory, Miss Gruber and her colleagues have not only developed some new methods, but also have shed some light on pickled stock in an area which we did not suspect before.

One of the things that always concerns us about new methods is how soon they will be applicable. Most of us take pH measurements for granted, but it is really not that many years ago that it was pretty difficult to measure pH, with a platinum-hydrogen electrode and the associated problems. I would like to ask Miss Gruber if there are any major obstacles in the application of these techniques right in the tannery.

MISS GRUBER: I don't see any right at the present time. Dr. Mellon went to a tannery recently and he took several different electrodes. He needed long lead wires to reach from the meter to the tannery vats. However, I think this could be readily done.

MR. CLINTON RETZSCH (Nopco-Diamond Shamrock): Miss Gruber, with regard to some of the differences which you noted, did you use commercial stock? If so, was any consideration given to the possibility that some preservative might be present which could cause some of the differences? Also, is it possible that surface-active agents might be present, but were not looked for in your analyses?

MISS GRUBER: These were commercially available hides which we secured from different tanneries. We did consider the possibility of preservatives or surface-active agents present in these hides. We did not feel that percentagewise these other anions and cations could contribute that much, since the sodium, chloride, and other ions are present in such great amounts.

MR. ALBERT S. JAMISON (Seton Leather Company): In your analysis you used silver chloride electrodes which tended to dissolve in the heavy brine solutions, and you mentioned that you changed them twice a day. Could you tell us what the cost of these electrodes is? Also, how do you know when to change electrodes?

MISS GRUBER: Offhand I don't know the cost of the electrodes. The electrodes were checked with a standard solution before and after each sample. Then, if the response was poor, we re-plated the electrode by putting a potential on it while immersed in a saturated potassium chloride solution. We reversed the potential about eight times, 30 seconds each time. Then, to test functionality, we placed it in a standard potassium chloride solution and measured the millivolts. The millivolts had to fall within a cetrain range for an electrode to be acceptable for use.

DR. EDWARD F. MELLON (Eastern Regional Research Center, USDA): The silver billet electrode which we used was a Beckman electrode costing about $25. Beckman also makes a silver/silver chloride solid state electrode costing about $150–$200. We found that either electrode could be used. The sintered solid state electrode is so much more costly, and we found that if we left it in a strong salt solution, the silver chloride portion would be dissolved out of the sinter. In a few months we had no electrode. Since this has happened to us, we have continued to use the silver billet electrode. Since it has a flat surface, it can be used on the surface of the hide.

Miss Gruber has mentioned my tannery visit. I also visited a hide curing plant. The chloride electrode did sense the correct concentration of the salt in the raceways of the curing plant. It also sensed the same sodium chloride concentration on the hide surface when the hides came out of the wringer; the hide surface values and the raceway values agreed. There is the possibility that this electrode could monitor the salt concentration in the raceway if we can support the electrode properly in the raceway. Thus, the operator could know the degree of salt saturation in his raceway brines.

DR. ROBERT M. LOLLAR (Consultant to the Tanners' Council): With reference to ammonia specific electrodes, please comment on the stability and other characteristics of the electrode, especially "poisoning" in such plant solutions as the raceway brines mentioned by Dr. Mellon or in tannery wastewaters.

MISS GRUBER: As far as stability is concerned, the samples take about 30 seconds to stabilize before recording the values.

For ammonia you would take a sample from the vat, dilute it, and then take a reading after adding ten molar sodium hydroxide. Then, after taking a reading on a standard solution, you get the difference. You then use this difference with a standard table to determine the millequivalents of ammonia. Samples for the

sodium ion electrode are also diluted, which should eliminate the possibility of "poisoning" the electrodes.

DR. MELLON: The ammonia electrode responds only to ammonia gas. The electrode contains a membrane which specifically transmits ammonia gas; therefore the electrode is very specific for free ammonia. It would measure any free ammonia in a solution, but in acid solutions this would be extremely small.

We are presently trying to show whether the ammonia electrode could be used to determine the ammonia produced from a Kjeldahl nitrogen analysis. The Orion people have done this, and claim that if a bank of five electrodes is used, considerable time can be saved in the Kjeldahl nitrogen determination. We are in the process of studying this for a large number of commercial leather samples. We hope to have the results for a *Journal* Technical Note before too long.